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ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

Vol. XIII

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No. 2

1—GENERAL AND PHYSICAL CHEMISTRY

1. On the dielectric constant of heavy water. T. Takéuchi. *Bull. Tokyo Univ. Eng.*, **7**, 419 (1938).—Relations between surface tension, solubility and dielectric const. of heavy water are described. Author.

2. On the study of porous substances. III. M. Kawakami and S. Uchida. *Bull. Tokyo Univ. Eng.*, **7**, 357—382 (1938).—Flow of water, air and a mixed gas of air and carbon dioxide through porous substances was investigated. Authors.

3. Structure of oxidized silicon film. H. Kamogawa. *Mazda Research Bull.*, **13**, 160—163 (1938), and *Phys. Rev.* **54**, 91 (1938).—Electron diffraction photographs were obtained by the transmission of electrons (0.058 to 0.063 Å) through thin films of silicon. The film is obtained by condensing silicon vapour on a polished rock-salt surface. The vapour is obtained from silicon metal which is heated electrically in a thorium crucible placed in a vacuum container. The free film is obtained by dissolving the crystal base in water. The diffraction pattern obtained by this film consists of three diffused rings corresponding to $(\sin \theta/2)/\lambda = 0.12$ (strong), $= 0.29$ (weak), $= 0.40$ (medium), which are quite different from those of silicon crystal. This result, somewhat similar to that of Maxwell and Mosley on a fused silica film, can be discussed as scattering from amorphous SiO_2 as previously treated by Warren. It may be concluded that a thin silicon film changes to an amorphous silica

film by spontaneous oxidation in air. Author.

4. Oiliness of liquid. J. Saneshima. *Nippon Gakujitu Kyoho*, **13**, 557—561 (1938).—The static and the kinetic boundary friction coeffs. of various liquids between the surfaces of glass or iron have been measured by several methods. The methods used for the measurements of the static friction were the "Balance method" and the "Inclination method". The former consists of the detn. of the tangential force to start the sliding motion of a slider on a lubricated surface by means of a prescription balance. This method is very simple and nonexpensive, while it gives accurate result. Measurements have been undertaken for the glass surfaces on aliphatic alcohols, fatty acids and hydrocarbons etc. In the case of aliphatic normal alcohols the friction coeffs. decrease by the increase of the number of carbon atoms in the molecule, thus from 0.68 for ethyl alcohol to 0.56 for n-octyl alcohol, while fatty acids give nearly const. value 0.59 from acetic to heptylic acid. This fact may be attributed to the greater affinity of COOH group to glass surface than OH group. The kinetic friction coeffs. have been detd. by the "Rotating cylinder method" and the "Sliding velocity method". The values are remarkably lower than the static friction coeffs., namely on alcohols 0.41—0.15 for glass surfaces, and 0.177—0.094 for iron surfaces. The static friction coeff. between clean dry glass surfaces was 1.04. This was lowered by the deposition of the monomole-

cular film of palmitic and oleic acid to 0.10 and 0.14 resp., while polymolecular layers of these substances show no further decrease in the friction. The liquid oleic acid in flooded state gives the value 0.29, which is far higher than in the case where the same substance exists in regular monomolecular layer. The static friction coeffs. of some mixed liquids have been measured. The nonpolar liquids have relatively high friction coeffs. for glass, but this lowered remarkably by the addition of a minute quantity of a polar substance. For example, the value for pure toluene is 0.76, which decreases to 0.43 by the addition of 0.1 % of oleic acid. This fact suggests us that the chemically impure technical lubricants will never give a definite and reliable value of friction coeff. Author.

5. Theories of diffusion, electric conductivity and viscosity. S. Kaneko.

J. Chem. Soc. Japan, **59**, 1093—1095 (1938).

—From Eyring's theory of reaction velocity, the following formulas of diffusion, electric conductivity and viscosity are obtained: $D = \frac{1}{6} k_1 \lambda^2 x = \frac{N e^2 z^2 c k_1 \lambda^2}{6 k T}$ $\eta = \frac{6 \lambda_1 k T}{\lambda^2 \lambda_2 \lambda_3 k_1}$ where

D is diffusion const., x specific conductivity, η viscosity, k_1 transition velocity, λ the distance between adjacent minima of potential, k Boltzmann's const., T absolute temp., λ_1 the distance between sliding molecular layers, λ_2 the distance between molecules in the sliding direction, λ_3 the distance between molecules in the vertical direction to λ_1 and λ_2 . The formulas of D and η have already been obtained by Eyring, but the number 6 is lacking in his equations. The above formula of viscosity is verified by the method different from Eyring's. Author.

6. Electrolytic winning of heavy

water. IV. T. Noguti. *J. Electrochem.*

Assoc. Japan, **6**, 299—303 (1938).—In the

preceding three reports, it was reported that, with iron, nickel and platinum electrodes in alkaline soln., the isotopic separation factor of deuterium from hydrogen is indifferent to almost

all the electrolysing conditions except in the electrolysis with the corroded electrode under superposition of alternating current at high temps. All the three electrode materials in the former case and iron and nickel electrodes in the latter case were also corroded and covered with gelatinous brown deposits. The platinum electrodes in the latter case were free from any trace of corrosion deposits even at a high temp. (57°C) and did not show any tendency of depression of the separation factor. From these exptl. facts, the author has proposed the suggestion that separation factor is not due to direct effect of temp. rise, but to the secondary effect of corrosion of the electrodes at high temps. In the present report, the exptl. verification for this suggestion is given. By continuously polishing the iron cathode surface with steel-wool brushes, about 70% or more of the depression of the separation factor at high temps. was successively recovered thus:

Temperature °C	2	20	30	40	50	57
Non-brushed iron cathode	5.5	5.1	4.6	4.2	3.6	3.2
Brushed iron cathode	5.5	5.4	5.2	5.1	4.8	4.6

From this table it will be seen that, though the depression of the separation factor at high temps. is almost recovered by brushing, yet there remains still a slight residue of depression.

Author.

7. Sound velocity in heavy water and compressibility. K. Yosioka. *Bull. Inst. Phys. Chem. Research*, **17**, 815—823 (1938),

and *Sci. Papers Inst. Phys. Chem. Research*, **34**, 843—853 (1938).—1) The sound velocity both in ordinary distilled water and in heavy water of $d_{20}^{20} = 1.1064$ was detd. at temps.

between 25°C and 90°C at a frequency of 4900 KC by the method utilizing the diffraction of light caused by the train of the sound waves. 2) The relation between the sound velocity and the temp. was found to be similar in both cases. The temp. at which the sound velocity becomes max. is higher in heavy water than in ordinary distilled water. 3) The relation between the adiabatic compressibility and the temp. was found also to be similar

in both cases. The temp. at which the adiabatic compressibility becomes min. is also higher in heavy water than in ordinary distilled water. 4) At 25.0°C, the sound velocity in pure D₂O was found by extrapolation to be 1398.6 m sec⁻¹, the adiabatic compressibility and the isothermal compressibility of pure D₂O 46.2₇ × 10⁻¹² dyne⁻¹ and 46.4₉ × 10⁻¹² dyne⁻¹ resp. Author.

8. **A method of ascertaining and defining fineness of powders.** I. Iitaka and R. Shiota. *Sci. Papers Inst. Phys. Chem. Research*, 34, 897—904 (1938).—A scale for grading comminuted powders has been developed which not only may be used within the range where standard sieves are available but is particularly useful for powders beyond this order. The mesh number is defined mathematically as a function of the distance between any two adjacent wires of a sieve and independent of the wire size, thereby eliminating the major source of discrepancy in sieves. The relation $m \cdot d = A$ (where m is the mesh number; d , the distance between two adjacent wires; and A , a constant) is the working formula for the construction of sieves. The constant A is a parameter detng. the wire space factor

for a set of sieves. In a set of standard sieves examined, A was found to be 0.579 in English units and 14.70 in metric units. A complete table of sieve specifications from 10 mesh to 1500 mesh calcd. by using $A=14.70$ is shown. For powders beyond the available range of sieves, grading is made possible by the graphical figures showing values of d calcd. with $A=14.70$ and multiplied by 100. The figures are for use with microphotographs at 100 diameter magnification.

Authors.

9. **On the reducing action of amalgams. VII. The mechanism of the reaction by shaking.** K. Masuda, *J. Chem. Soc. Japan*, 59, 1280—1284 (1938).—In the quiet state, the reducing quantity, Q increases with the hydrogen ion conc., $[H^+]$, of the soln.: the relation between Q and $[H^+]$ is represented by $Q = a + b[H^+]$, where a and b are consts. By shaking, however, Q decreases as $[H^+]$ is increased: this should be attributed to the hydrogen bubbles, formed at the time of shaking, by which the interface reaction is disturbed. From the analytical results, the coeff. of formation of hydrogen bubbles is shown to be proportional to $[H^+]$ of the soln. Author.

2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

10. **Co-ordinate valency rings. III. Some inner complex salts of iron and manganese.** T. Tsumaki. *J. Chem. Soc. Japan*, 56, 1329 (1935); *Bull. Chem. Soc. Japan*, 13, 579—582 (1938).—By means of the reaction between hot soln. consisting of salicylaldehyde, ammonia and alcohol, and aqueous soln. of iron ammonium alum, the red brown ppts. were obtained. By recrystallization of the ppts. from nitrobenzene, trisalicylaldehyde-diimine-iron, $C_{21}H_{15}O_3N_2Fe$,

was isolated. Trisalicylaldehyde-diimine-manganese, $C_{21}H_{15}O_3N_2Mn$, salicylaldehyde-benzylimine-manganese, $C_{28}H_{24}O_2N_2Mn$, and salicylaldehyde-benzylimine-manganic hydroxide, $C_{28}H_{22}O_5N_2Mn \cdot 2H_2O$ were also obtained. **IV. Inner complex cobalt salts of hydroxyaldimines.** *ibid.*, 58, 1288—1294 (1937); *Bull. Chem. Soc. Japan*, 13, 252 (1938).—The reddish brown salicylaldehyde-ethylenediimine-cobalt (Ann. 1933, 824)

is stable in absence of air, but it absorbs oxygen in air to yield a black oxide, which regenerates the reddish brown cobalt salt at 100° . A solvate, salicylaldehyde-ethylenediimine-cobalt + CHCl_3 , which forms dark red prisms, regenerates the reddish brown salt at 100° and gives in air especially easily the black oxide. The mode of the loose combination of oxygen with the inner complex salt is considered to be analogous to that of the combination of oxygen molecule with the iron atom in oxyhaemoglobin. The reddish brown cobaltous salt, when kept in chloroform in air, gives the dark violet salicylaldehyde-ethylenediimine-cobaltic hydroxide, $(\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{Co})\text{OH}$, which gives by treating it with ammonium chloride in methyl alcohol the dark brown salicylaldehyde-ethylenediimine-cobaltic chloride, $(\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{Co})\text{Cl}$. The extinction coeffs. of salicylaldehyde-ethylenediimine-cobalt, its oxide, and the hydroxide were measured. The absorption curves of these compds. indicate that the oxygen atoms in ligands are trans to each other, thus necessitating the asymmetric structure for these compds.

Author.

11. Spectrochemical study of microscopic crystals. I. Application of microscopes in spectrography. R. Tsuchida and M. Kobayashi. *Bull. Chem. Soc. Japan*, **13**, 619—623 (1938).—A new method of measuring absorption spectra of microscopic crystals is proposed. Application of a polarizing microscope renders it possible to measure pleochroism of microcrystalline substances. An example of cis-dichloro-tetrammine-cobaltic chloride is shown.

Authors.

12. Absorption spectra of co-ordination compounds. I—II. R. Tsuchida. *Bull. Chem. Soc. Japan*, **13**, 388—400; 436—450 (1938).—The origins of absorption bands of co-ordination compds. are discussed. The absorption spectra of co-ordination compds. consist of the 1st, and 2nd and the 3rd bands as well as those due to ligands themselves. Some of the compds. may lack

the 1st or the 3rd, or both the bands, but none of them lacks the 2nd. The 1st band is attributed to electron transitions in the unsaturated transition shell of the central ion. The band, therefore, appears only when the central ion is of a transition element. The 2nd band may be attributed to co-ordination electrons, and is, therefore, the most general characteristic of a co-ordination compd. The origin of the 2nd band is a kind of reversible dissocn. of ligands. The 3rd band is explained due to a kind of neutralization between the central ion and a ligand anion and the neutralization takes place only in the compds. which have a pair or pairs of negative radicals in trans-co-ordinations. Besides these numbered bands, a co-ordination compd. has generally some bands due to ligand themselves, which are here termed as special bands. The special band of a ligand is, in most cases, shifted towards the longer wave lengths compared with the absorption band of the ligand in free state. The stability of co-ordination compds. is explained in terms of the spectrochemical series of ligands which are deduced from the wave-lengths of the 2nd band.

Author.

13. Absorption spectra of co-ordination compounds. III. Special bands of chromium complexes. R. Tsuchida and M. Kobayashi. *Bull. Chem. Soc., Japan*, **13**, 471—480 (1938).—Absorption spectra of several chromic complexes were measured. It was found that the spectrochem. series of ligands for chromic ion is coincident with that for cobaltic ion. From the spectrochem. series is discussed the stability of the chromic complexes and some of the methods of prepn. are explained. All the chromic complexes have the 1st and 2nd bands. $[\text{Cr}(\text{NH}_3)_5\text{NCS}]$ (SCN)₂ has another band in addition, which is due to the group $\text{M} \leftarrow \text{N}=\text{C}$, where M is a metal-ion of any kind and valency. $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]\text{NH}_4$ and $[\text{Cr}(\text{NCS})_6]\text{K}_3$ have four bands each, the 1st, the 2nd, the special and the 3rd. The special bands are attributed to the same origin as that of $[\text{Cr}(\text{NH}_3)_5\text{NCS}]$

X_2 and the 3rd band is due to trans-pairing of the anions. Chromate ion, a quadri-coordinate complex, has not the 1st band, but has the 2nd and the 3rd, as could be expected from the author's hypothesis. Absorption spectra of polynuclear complex may be analysed into those of component complex radicals. For example, $[Co(NH_4)_5CrO_4] Cl$ has three bands, one of which is the 1st band of the sexa-co-ordinate cobaltic complex and the other two are mainly the 2nd and the 3rd bands of the quadri-co-ordinate chromate radical. The 2nd band of the former is almost entirely covered by the 2nd band of the latter.

Authors.

14. **Intervals of X-ray spin-doublets.** G. Araki and S. Noma. *Proc. Phys.-Math. Soc. Japan*, 20, 746—754 (1938).—The intervals of the X-ray spin-doublets are calcd. for the L, M, and N terms of Cl, K, Ca, Cu, Rb, and Cs atoms, on the basis of the Breit Hamiltonian formula. The eigenfunctions used in the computations involve the Hartree or the Hartree-Fock radial functions. The agreement between the calcd. and the observed values is satisfactory in general.

Authors.

15. **Electronic states of divalent metals.** K. Ariyama. *Sci. Papers Inst. Phys. Chem. Research*, 34, 344—356 (1938).—According to the electron theory of metals the valence electrons of the divalent metals belong to two energy bands which energetically overlap. Under the assumption that the overlapping is small and that the pos. holes in the lower band as also the electrons in the upper band behave as "nearly free electrons", the free-electron-number (Freiheitszahl), numbers of pos. holes and electrons, etc. were detd. half-empirically for Be, Mg, Zn, Cd and Hg of the formulae for the conductivity at high temps., for the Hall-coeff. and for the change of resistance in a magnetic field and of the corresponding measurements. The magnetic susceptibilities calcd. from the formulae of Pauli and Peierls with the above values of consts. agree with expts. in the order of magnitude.

Author.

16. **On the energy states of valency electrons in some metals. Selectivity of photo-electron transition in zinc, and the selection rule, $\Delta l = \pm 1$.** M. Satō. *Nippon Kinzoku Gakkai-Si.*, 2, 394—400; *Sci. Repts. Tohoku Imp. Univ.*, I, 27, 137—154 (1938).—The selectivity of photo-electron transitions in the surface of zinc crystal was closely examd., and it was found that it has an intimate relation with the direction of the oscillating electric vector of the exciting light. Applying the results obtained from the electrode potentials of the surfaces of Zn-single crystal, it is inferred that the selection rule, $\Delta l = 1$, is explicable from the fact that the stability of orbital motion of the electron depends on the mutual orientation of the orbital plane and the electric vector of the exciting light. On the basis of this conception it is concluded that the orbital planes of p and d electrons in the energy levels, E_2 and E_3 , in the surface layer of zinc crystal are perpendicular and parallel resp. to the axis $[0001]$ of the crystal of this metal.

Author.

17. **A contribution to the theory of the hydrogen molecule.** T. Inui. *Proc. Phys.-Math. Soc. Japan*, 20, 770—779 (1938).—The energy for the ground state of the H_2 -molecule was calcd. by various methods from the wave function involving two parameters α and β . The chosen orbital function for the ground state has the form: $\Psi(1,2) = \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)$, where $\psi_a(i) = e^{-\alpha r_i - \beta \eta_i}$ and $\psi_b(i) = e^{-\alpha r_i + \beta \eta_i}$ ($i=1, 2$), ξ and η are the spheroidal co-ordinates defined by the relations $\xi = \frac{ra+rb}{R}$

and $\eta = \frac{ra-rb}{R}$ where R denotes the inter-nuclear distance, and ra and rb are the distances of an electron from the nuclei a and b resp. If this expression is assumed, the energy formula is reduced (without neglection) to a rather simple form: $E = 2a(\alpha, \beta)k^2 - b(\alpha, \beta)k$, $k = 1/R$, $a(\alpha, \beta)$ and $b(\alpha, \beta)$ being expressions involving several molecular integrals. The binding energy calcd. was 4.043 e.V. which

is to be compared with the value 4.72 e. V., obtained from the expt. the equil. distance and fundamental vibration frequency were calcd., yielding the values 0.757 Å (exp. 0.740 Å) and $4.39 \times 10^3 \text{ cm}^{-1}$ (exp. $4.318 \times 10^3 \text{ cm}^{-1}$) resp. The conception of orbitals and the Hartree-Fock approximation method for the present molecular system are discussed.

Author.

18. **On the Interaction of elementary particles. IV.** H. Yukawa, S. Sakata, M. Kobayasi and M. Taketani. *Proc. Phys.-Math. Soc. Japan*, III, 20, 720—745 (1938). — In previous three papers, Yukawa and others developed the theory of the heavy quant. to explain the exchange force between the proton and the neutron. In this paper, the authors show, first, that it is necessary to introduce the neutral heavy quant. for the explanation of the fact that the force between like particles is approximately equal to that between unlike particles. And, it is shown that the force between unlike particles as well as the force between like particles thus obtained is not strictly central, so that there is the complicated coupling between the stationary states of the nuclear system, even in the deuteron problem. Moreover, on account of the fact that the potential between two particles involves the terms which are proportional to $\frac{1}{r^2}$ and $\frac{1}{r^3}$ at small distance r , one can not solve the deuteron problem rigorously. This difficulty, however, is not very essential, since the applicability of the present theory must be restricted to the case where the distance of the particles is not so small compared with $\frac{1}{\kappa}$. Next, the theory of β -disintegration is developed according to the vectorial field theory, and it is shown that the theory constructed in the suitable way leads to the distribution of β -ray which is equivalent to the combination of those of Fermi and Konopinski-Uhlenbeck, but, it gives the life time of the heavy quant. which is too short to explain the cosmic ray hard component, as long as the interac-

tion of Konopinski-Uhlenbeck is included in appreciable amount. The probability of the creation of heavy quanta by photons in matter is also estimated by assuming the scalar field theory for heavy quanta, and the possibility that the hard component of cosmic ray consists of heavy quanta thus produced is discussed. The problem of the spin and the magnetic moment of the heavy quant. is discussed in detail.

Authors.

19. **Infra-red absorption spectra and molecular structures of polar liquids.** T. Sidei. *Gakujitu Kyoto*, 13, 336—339 (1938). — Infra-red absorption spectra of some polar liquids which contain the OH group were studied in the region between 1.0μ and 2.5μ . The spectra of water, alcohols, sulphuric acid and carbonyl acids were observed at various temps. Acid salts in crystalline and fused states and crystals of hydrated metal sulphates were also studied. The OH bands of these liquids were markedly modified and new bands were always observed at the higher frequency side accompanied by the fading of the original lower temp. bands at the lower frequency side when samples were heated. This phenomenon was ascribed to the existence of the quasicrystalline liquid lattice which is bounded by the hydrogen bridge bond and its modification by the change of temp. In the case of water of crystallization, the bands were modified corresponding to their O-O distance in hydrogen bridges. For acid salts the bands characteristic of the OH group were not observed in the crystalline state, but OH bands similar to those of acids appeared in the fused state. The lower limit of the OH band first observed was a diffuse one with a maximum near 1.8μ which was observed in acids at lower temp. and in crystals of alums. As the O-O distance increased or the intermolecular binding weakened, the OH band displaced toward the higher frequency side with the upper limit near 1.4μ . These modifications of OH bands were attributed to the predominance of the polar character in the binding

between O and H as the intermolecular hydrogen bond strengthened. The nature of the hydrogen bridge is discussed in connection with the Raman effect on carbonyl acids.

Author.

20. **The near-infrared spectrum of cadmium. I.** O. Masaki and K. Kobayakawa. *J. Sci. Hiroshima Univ.*, A, 8, 289—291 (1938).—The near-infra-red spectrum of cadmium was photographed as far as 12000 Å. The light source was H-shaped Geissler tube. The plates were infrared sensitive 1—% plates, which were first sensitized by the ordinary manner, and then made more sensitive by heat treatment. Authors.

21. **On the quantum theory of the phosphorescence of crystalphosphor. II.** T. Muto. *Sci. Papers Inst. Phys. Chem. Research*, 33, 5—25 (1937).—In the previous paper (Part I), we have developed quantum-mechanically the theory of the phosphorescence in crystalphosphor, using the modifications of Wilson's semiconductor model, and the long afterglow characteristic of the phosphorescence has been attributed to the existence of the metastable states in the foreign atoms involved. Since the previous model was too much simplified, we have, in the present paper, improved the crystal model in accordance with the exptl. facts and discussed quantum-mechanically the phosphorescent process of the new model along a similar line as before. Since the alkali-halide phosphors are simple in structure, we have discussed in detail the decaybehaviour and temp. dependencies of their "Lichtsumme" of phosphorescence, and compared with Bürger and Flechsig's expt., getting satisfactory agreements. Further, we have discussed qualitatively the characteristic temp. dependencies of the various kinds of phosphorescent substances, which can be prepared in the crystalline state. Finally, we have proposed the possible models of crystalphosphor, taking into consideration the localized levels of the trapped electron

originated by Frenkel, and discussed quantummechanically their phosphorescent process, getting agreements with the exptl. observations. In summing up the results of Part I and II, it may be concluded that the characteristics of the phosphorescence are to be essentially controlled by the localized electronic levels, which may occur within the foreign atoms as well as in their distorted neighbourhood. Author.

22. **The multiple structure of the electron.** U. Kakinuma. *Sci. Papers Inst. Phys. Chem. Research*, 34, 991—1000 (1938).—A stationary electron has a multiple structure of spherical symmetry. The innermost core of radius $\sqrt{\hbar^2/mc^2}$ or $\sqrt{\hbar^2/C^2}$ ($=10^{-30}$ cm). contains the electronic mass and charge. The outer region extending from $c^2/2mc^2$ to infinity is the ordinary electromagnetic field in which the energy mc^2 is stored. The intermediate region has not yet been explored. The quantum mechanics deals with the state of these fields superposed altogether. The energy in the core is composed of two parts: the one is of the fixed value corresponding to the spin magnetic energy, and the other is of a variable amount sharing the kinetic energy with which the electron describes a certain Bohr orbit. The spin angular momentum is identified with the intrinsic action of the electron, viz. $\hbar/2$. The corresponding magnetic moment is calcd. classically, obtaining the correct value $\hbar/2 \cdot e/mc$. Author.

23. **On the bands of the aluminium fluorite (AlF).** T. Yuasa. *Sci. Repts. Tokyo Bunrika Univ.*, A, 3, 239—248 (1938).—The vapour of the aluminium fluoride (AlF₃) or the cryolite is excited in a Geissler tube by heating to 200°C at the pressure of 2~3 cm Hg. There is found a band system degraded towards the longer wave-length side in the near ultra-violet region ($\lambda\lambda$ 4176.64 Å~3187.61 Å), which is considered to belong to AlF. As the result of the vibrational analysis of these bands, the molecular constants $x_e\omega_e$ and ω_e were obtained as 27.8 cm⁻¹ and 7.08.6⁻¹ resp. for the upper

level and 1.3cm^{-1} and 698.6cm^{-1} for the lower level. The nuclear distance calcd. with these const. is about 1.625 \AA . This value is just between 1.59 \AA and 2.259 \AA which are the nuclear distances of the silicon nitride (SiN) (the electron number, 21) and the silicon fluoride (SiF) (the electron number, 23) resp. This is also roughly equal to 1.62 \AA , the nuclear distance of the silicon oxide (SiO) (the electron number, 22). So this is an isoelectronic molecule of AlF. Author.

24. **The β -ray spectrum of RaE.** Y. Watake and J. Itoh. *Proc. Phys.-Math. Soc. Japan* 20, 809—813 (1938).—The β -ray spectrum of Ra-E was measured by magnetic focussing method. The radius of electron pass was 10 cm and the angular spread of electron was 6° , the resolving power of the spectrograph being very high. The result of the expt. was briefly as follows: The general shape of the spectrum agreed with the theory of Konopinsky and Uhlenbeck, while at the vicinity of upper limit, the exptl. points fall appreciably below the K. U. curve. Thus it must be assumed that the neutrino mass is not zero but about 0.4 of electron mass, provided that the theory of K—U is the true one. The extrapolated K—U upper limit was 3.67 mc^2 , while the inspection upper limit was 3.27 mc^2 .

Authors.

25. **Absorption spectra of salicylaldehyde-ethylenediimine and related compounds.** R. Tsuchida and T. Tsumaki. *Bull. Chem. Soc. Japan*, 13, 527—533 (1938).—Absorption spectra of benzaldehyde-ethylenediimine, o-methoxy benzaldehyde-ethylenediimine, salicylaldehyde-ethylenediimine and o-hydroxyacetophenone-ethylenediimine were measured, and the structure of the spectra is explained qualitatively by the theories of absorption spectra of co-ordination compds. The longest-waved band of salicylaldehyde-ethylenediimine as well as of o-hydroxyacetophenone-ethylenediimine is explained as due to intramolecular formation of a hydrogen bridge between the hydroxyl group and the nitrogen atom. In other words, an absorption band of

a hydrogen bond is found in the near ultra-violet region. The absorption spectrum of salicylaldehyde-ethylenediimine-cobalt is also explained and the steric configuration of the inner complex is thereby corroborated.

Authors.

26. **Absorption spectra of metallic complex salts of 2,2'-Dipyridyl. II.** K. Yamasaki. *Bull. Chem. Soc. Japan*, 13, 538—542 (1938).—The absorption spectra of 2,2'-Dipyridyl in hexane and water, and those of $[\text{Mn}(\text{Dip})_2]\text{Cl}_2$, $[\text{Co}(\text{Dip})_2\text{CO}_3]\text{Cl}$ and $[\text{Co}(\text{Dip})_2\text{Cl}_2]\text{Cl}$ (Violet) in water were studied between 220 and $700\text{ m}\mu$. Dip means 2,2'-Dipyridyl molecule. The decomposition of $[\text{Mn}(\text{Dip})_2]\text{Cl}_2$ in dilute soln. was confirmed from the absorption spectra. Compared with the absorption band of $[\text{Co}(\text{Dip})_2]\text{Cl}_3$, those of $[\text{Co}(\text{Dip})_2\text{CO}_3]\text{Cl}$ and $[\text{Co}(\text{Dip})_2\text{Cl}_2]\text{Cl}$ in the visible region displace toward the longer wave length. (Cf. I. *Bull. Chem. Soc. Japan*, 12, 390 (1937)).

Author.

27. **Studies on fluorine at low temperatures. X. (1) The colour of liquid fluorine. (2) Photochemical reaction of liquid fluorine and liquid oxygen. (3) A new compound: 2-3 oxygen fluoride O_3F_2 .** S. Aoyama, and S. Sakurada. *J. Chem. Soc. Japan*, 59, 1321—1328 (1938).—Pure fluorine is colourless or pale yellow in the liquid state, and snow white in the solid state. Golden yellow colour of liquid fluorine is due to impurities such as oxygen fluoride dissolved in it. Liquid fluorine kept in glass vessel at low temp. reacts with the components of its container. I.e., alkali, silicon, calcium and oxygen combined with these elements; these reactions are accelerated by the aid of ultra violet ray. By exposing a mixture of liquid fluorine and liquid oxygen to ultra violet ray a new compd. of oxygen fluoride crystallizes out as deep reddish brown crystals whose chemical formula corresponds to O_3F_2 . It is deep blood red in the liquid state and melts at $-177^\circ\sim-180^\circ\text{C}$. This compd. decomposes into O_3F_2 and O_2 when

it is warmed slightly at a low temp. and then into F_2 and O_2 at room temp. By photochemical reaction the solid crystal ($-196^\circ C$) is transformed to the liquid state and then decomposed to F_2O_2 (Solid) and oxygen gas. These transformations and decompositions are now under investigation.

Authors.

28. **Absorption bands of metallic complexes. IV. Special bands of nitroammine cobaltic complexes.** H. Kuraya and R. Tsuchida. *J. Chem. Soc. Japan*, **59**, 1142—1144 (1938).—Absorption spectra of co-ordination compd. generally consist of the first, the second and the third bands. They may, however, have also a few special bands due to ligands themselves. Absorption spectra of several nitroammine cobaltic complexes were measured and the special band is explained as the second band of NO_2 group. The stability of the NO_2 group as well as the complex as a whole is discussed in terms of the frequency of the second band. Authors.

29. **Absorption spectra of rhodanates of metals. II. Rhodanate complexes of molybdenum.** Y. Uzumasa and K. Doi. *J. Chem. Soc. Japan*, **59**, 1047—1052 (1938).—The absorption spectra of $K_2MoO(SCN)_6$ and $K_3Mo(SCN)_6$ in water, alcohol, acetone and ether+alcohol were observed. They were compared with corresponding chloro-complexes, i. e., K_2MoOCl_5 and K_3MoCl_6 . When Mo is in the quinquivalent state, SCN^- shows as expected a bathochromic effect, while when the element is in the trivalent state the chloro-complex develops a deeper colour than the rhodanate-complex. A band at 2850\AA which has been considered to be characteristic for rhodanate-complexes can not be found in the Mo

rhodanate-complexes. It is also found by the electrolytic and spectroscopic examn. that Mo is most hyperchromic when the metal is in the quinquivalent state. Authors.

30. **On the molecular spectra $^2H \rightarrow ^2\Sigma$ of mercury hydride and deuteride. I— $^2\Sigma$ State.** Y. Fujioka and Y. Tanaka. *Sci. Papers Inst. Phys. Chem. Research*, **34**, 713—740 (1938).— $^2H_1 \rightarrow ^2\Sigma$ and $^2H_2 \rightarrow ^2\Sigma$ bands of HgH and HgD are photographed and analyzed using the second order spectra of a 6-meter concave grating. The consts. of the lower $^2\Sigma$ states are calcd. till $v=3$ for HgH and till $v=4$ for HgD . The spin doubling of the $^2\Sigma$ state is remarkably large, and for its separation const. F_v we obtain an empirical formula $F_v = a_v + b_v \left(K + \frac{1}{2} \right)$.

It is remarkable that the ratio $\frac{a_{v,D}}{a_{v,H}}$ for $v=0$ gives 0.5037 ± 0.0011 , which agrees with theoretical ρ^2 in the limit of the probable error. The calcd. B_v shows that the variation of them against v is so large that it is hardly reliable to use the usual expansion formula for them. Still the calcn. of B_e gives $B_{e,H} = 5.5490 \pm 0.0027$, $B_{e,D} = 2.7989 \pm 0.0029$ and $\frac{B_{e,D}}{B_{e,H}} = 0.5044 \pm 0.0006$. Although this value is not in good agreement with $\rho^2 = 0.5039$, we can not conclude the invalidity of the theory because of the above-mentioned circumstance. The calcn. of the vibrational const.

$4G_v + \frac{1}{2}$ gives very rapid decrement for increasing v in the case of HgH as compared with that of HgD . Indeed the use of the expansion formula for G_v gives improper sign for $y_e\omega_e$ in the case of HgH ; therefore, it is impossible to discuss about the theory of isotope effect in this case. Authors.

3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

31. **On the electric conductivity and dielectric constant of mixture.** S.

Kaneko. *Bull. Electrotech. Lab.*, **2**, 669—671 (1938).—The properties of linear function and

the method of detng. const. in the function are considered and this result applied on Fricke's equation expressing the electric conductivity and dielectric const. of mixt. which is also a linear function of compn. Further it is verified that Fricke's and Wiener's equations express the same relation and the characteristic properties of these equations are cleared up.

Author.

32. Theory of electrolytic conduction. S. Kaneko. *Bull. Electrotech. Lab.* 2, 664—666 (1938).—On application of the theory of reaction velocity by Horiuti (*Bull. Chem. Soc. Japan*, 13—210 (1938).) the following formulas of specific conductivity of electrolytes are obtained:

$$\kappa = \frac{1}{6} N c k_1 \left(e^{\frac{\epsilon x F \lambda}{RT}} - e^{-\frac{\epsilon x F \lambda}{RT}} \right)$$

$$\text{and } k_1 = \sqrt{\frac{kT}{2\pi m}} \frac{a\pi\lambda^2}{v_f} e^{-\frac{U^*}{kT}}$$

where κ is specific conductivity, N Avogadro's number, c concn. of the ion, k_1 number of jumps per unit time, ϵ the charge of an electron, z ionic valency, λ the length of one jump, k Boltzmann's const., T absolute temp., a transmission coeff., v_f free volume of an ion, U^* activation energy. From the above relations, the empirical formulas of Rasch—Hinrichsen and Poole are deduced.

Author.

33. Electric dissociation of biguanide in aqueous solution. K. Sugino and M. Ogawa. *J. Electrochem. Assoc. Japan*, 6, 292—298 (1938).—Biguanide ($\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{NH}_2$) is a diacidic base which is easily prepared from calcium cyanamide. In order to det. basic properties of this compd. the electric conductivity of aqueous soln. of biguanide (conc. range: 0.2~0.001 mol/l.) and of biguanide mononitrate (conc. range 0.02~0.0001 mol/l.) was measured at 25°C. From these data, values of A_∞ , of $\text{I}_{\text{RON}+}$, and of the degree of primary disocn.

$\left(\frac{A}{A_\infty}\right)$ for biguanide ($\text{B}(\text{OH})_2 \rightleftharpoons \text{BOH}^+ + \text{OH}^-$, $\text{B}=\text{biguanide}$) were calcd. to be $A_\infty =$

234, $\text{I}_{\text{RON}+}=39$, $\left(\frac{A}{A_\infty}\right) = 0.626$ (0.1mol/l.), 0.722 (0.05), 0.872 (0.01), 0.928 (0.004), 0.959 (0.001) resp. Values of $\left(\frac{A}{A_\infty}\right)$ seem to be almost comparable with that of $\frac{1}{2}$ Ba

$(\text{OH})_2$ and biguanide, like guanidine is an exceptionally strong base among organic bases. Detn. of " k_2 " of biguanide (disocn. const. of secondary OH) was also carried out. For this purpose, methods of conductometric titration and of potentiometric titration of aqueous soln. of biguanide by strong acids were used and the former gave satisfactory result. " k_2 " was calcd. by the following formula which was newly derived: $k_2 = -\frac{10^{-14}(\frac{dA^*}{dc})_{c=0}}{(\text{I}_{\text{H}^+} - \text{I}_{\text{RON}^+})}$, where A^* is the molecular conductivity of biguanide disalt and $-(\frac{dA^*}{dc})_{c=0}$ is easily found from the $A^* \sim \sqrt{c}$ curve of biguanide disalt. Values " k_2 " obtained by different methods almost coincided together, and taking the mean value, " k_2 " was detd. to be 2.24×10^{-10} .

Authors.

34. On the electrode potential of the carbon electrode of air cell and hydrogen ion concentrations. S. Makino and J. Yoshida. *Bull. Electrotech. Lab.* 2, 826—830 (1938).—The relation between the electrode potential of the carbon electrode of air cell and hydrogen ion concns. of electrolyte was investigated. As the samples, Furukawa's and Lecarbon's electrodes and Clark-Lubs' buffer soln. from pH₃ to pH₁₀ were used. The electrode potential, obtained within a range of pH from 3 to 6 is shown approximately as a linear function of pH.

Authors.

35. On the measurement of pH value. S. Kaneko. *Bull. Electrotech. Lab.* 2, 718—721 (1938).—In the former report individual activity coeffs. in the mixed electrolytes are expressed as a function of mean activity coeffs. by the following equation:

$$\ln f_{\pm}/z_{\pm} = \sum_i t_i^0 \frac{(z_i - z_{\pm})}{z_{\pm} z_i} \ln T_{\pm i} - \sum_i t_i^0$$

$$\begin{aligned} \frac{(z_\alpha - z_\beta) \ln r_{\alpha\beta}}{z_\alpha z_\beta} - \sum_\eta t_\eta^\alpha \frac{(z_\alpha - z_\eta) \ln r_{\alpha\eta}}{z_\alpha z_\eta} \\ \ln f_\beta/z_\beta = - \sum_\eta t_\eta^\alpha \frac{(z_\alpha - z_\eta) \ln r_{\alpha\eta}}{z_\alpha z_\eta} + \sum_\eta t_\eta^\alpha \\ \frac{(z_\alpha - z_\beta) \ln r_{\alpha\beta}}{z_\alpha z_\beta} + \sum_x t_x^\alpha \frac{(z_x - z_\beta) \ln r_{x\beta}}{z_x z_\beta} \\ t_x^\alpha = \frac{m_x z_x}{\sum m_x z_x^2 + \sum m_\eta z_\eta^2} \\ t_\eta^\alpha = \frac{m_\eta z_\eta^2}{\sum m_x z_x^2 + \sum m_\eta z_\eta^2} \end{aligned}$$

where m , z , f denote molarity, ionic valency and individual activity coeff. resp., subscripts x and η denote any positive and negative ions resp. α and β denote special positive and negative ions resp. and $r_{x\eta}$ denotes the mean activity coeff. of the salt $x\eta$. From the above relations, the methods of detng. pH value are discussed.

Author.

36. On the theory of the thermoelectric properties of alloys. T. Muto. *Sci. Papers Inst. Phys. Chem. Research*, 34, 741—750 (1938).—According to the electron theory of metal, the absolute thermoelectric power S of metals and alloys may be written, at temperatures above θ .

$$S = \frac{\pi^2}{3} \frac{k^2 T}{e} \left\{ \frac{2}{k \frac{dE}{dK}} + \frac{\frac{d^2 E}{dK^2}}{\left(\frac{dE}{dK} \right)^2} + \frac{\frac{d\tau}{\tau K}}{\frac{dE}{\tau dK}} \right\}_{E=S}$$

where T is the absolute temp., k the Boltzmann const., e the electronic charge and K an absolute value of wave number vector on the Fermi-surface. E expresses the elec. Fermi energy, S the Fermi Energy and τ the time of relaxation which depends on K . Now Nordheim has shown quantum-mechanically that the expression for τ or alloys has the form of $1/\tau = 1/\tau_0 + 1/\tau_T$ at temps. above θ , provided the alloy consists of a single phase. τ_T is due to the thermal vibrations of atoms situated at lattice points, and τ_0 due to the alloy-formation from different kinds of atoms, the residual resistance being inversely

proportional to τ_0 . Through the quantities τ_0 and τ_T , therefore, the absolute thermoelectric power depends on the atomic concn. of the component metals of an alloy. This is discussed in detail and compn. is made with experimental results. Furthermore, the thermoelectric power of dilute solid solutions of the noble metals is dealt with and a simple relation between the thermoelectric power and the residual resistance is obtained in accordance with the experimental observations. And also the reasons are pointed out for the fact that the thermoelectric power of the noble metals is positive in sign, whereas the sign of the alkali metals is negative.

Author.

37. On the Volta effect between pure metals. S. Kaneko. *Bull. Electrotechn. Lab.*, 2, 722 (1938).—It is verified that the Volta effect between pure metals must be null from thermodynamical reasoning.

Author.

38. On the transition point of calcium sulphate in water and concentrated sea water. T. Toriumi and R. Hara. *Techn. Rep. Tohoku Imp. Univ.*, 12, 72—90 (1938).—The transition points among $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and CaSO_4 (insol.) in pure water and in the concd. sea water at various concn. were measured by various methods, and the range of temp. and of the concn. of the sea water where only $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystallizes out is discussed. Also, the transition point data of calcium sulphate in pure water, as cited generally from the results of van't Hoff and his co-workers, are pointed out as invalid. And from the vapour press. of conc. sea water and the above results, the dissoen. press.-temp. equation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ are derived anew. Then the heat of hydration, the free energy change and variation on the forms of calcium sulphate were discussed.

Authors.

39. On the calcium sulphate in sea water II. Solubilities of calcium sul-

phate hemihydrate in sea water of various concentrations at 65-150°C. T. Toriumi, T. Kuwahara and R. Hara. *Technol. Rep. Tohoku Imp. Univ.*, **12**, 60-71 (1938).—Though the occurrence of hemihydrate is frequently observed at the real scale formation in brine evaporators, this form of calcium sulphate is always either unstable or metastable, and never stable, in the brines of any concn. and any temp. In a certain temp. range which is not very far from the transition point of hemihydrate into dihydrate, however, the velocity of the transformation

being comparatively slow, the solubility detn. for this salt is possible, and it was carried out by the present authors in the temp. range 65 ~150°C. at the brine concn. varied from the normal sea water to the concn. 97 g Cl/1000 g brine (about 6 times normal sea water concn.) As in the case of dihydrate and anhydrite, calcium hemihydrate also is likely to disintegrate into very fine crystals which give no definite solubility data. The authors paid special care to prepare the hemihydrate crystals which hardly undergo disintegration.

Authors

4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

40. Sedimentation volume and thixotropy. H. Akamatsu. *Bull. Chem. Soc. Japan*, **13**, 456-462 (1938).—The apparent volume of the powder pptd. in the liquid medium, i.e. sedimentation volume of the powder was measured. In general, when the powder is a polar substance, the sedimentation volume in nonpolar liquid is always larger than that in polar liquid. On the other hand, if the powder is nonpolar as graphite, there is no disparity in the sedimentation volume according to the nature of the liquid. Addition of a small amount of the polar substance decreases the sedimentation volume remarkably in the nonpolar solvent. A system which has the large sedimentation volume shows always marked thixotropic nature. Such a powder as glass, talcum, zinc oxide, calcium carbonate, makes a thixotropic system in the nonpolar liquid such as benzene, toluene, hexane, carbon tetrachloride. Furthermore such

a thixotropic nature as this is destroyed, if a very small amount of a polar surface active substance is added.

Author.

41. The thixotropic and plastic behaviour of suspensions of barium sulphate with clay. B. Tamamushi and Y. Sekiguchi. *Bull. Chem. Soc. Japan*, **13**, 556-565 (1938).—(1) Non-thixotropic suspensions of BaSO_4 become thixotropic on adding certain amounts of a sodium-clay formed from a natural hydrogen-clay. 2) The plasticity of the suspensions of BaSO_4 increases when the sodium-clay is added. 3) The correlation among thixotropy, loose packing of particles (large volume of sedimentation), and isothermal plasticity, which is now generally accepted, is evident also in systems under investigation. 4) A characteristic influence of the particle size of BaSO_4 on thixotropy and plasticity of the systems is mentioned.

Authors.